Quantum chemical study of the reactions of H_2 and H_2O molecules with $N_2(A^3\Sigma_u^+)$

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Molecular nitrogen excited to the lowest triplet electronic state $A^3\Sigma_u^+$ is quite interesting species for the following reasons: (*i*) it has rather high radiative lifetime (≈ 2 s) and (*ii*) its electronic excitation energy (T_e=6.22 eV) exceeds the energy barriers for many endoergic chemical reactions that indicates a potentially high reactivity [1]. Elementary reactions with $N_2(A^3\Sigma_u^+)$ molecules participate in the nitrogen and nitrogen-oxygen discharge plasma chemistry, play an important role in the atmospheres of different planets and in high-enthalpy flows [2-4]. The reactions of $N_2(A^3\Sigma_u^+)$ that can be easily produced in a specially arranged electric discharge with small H_nO_m species are also of special interest because of their possible crucial role for plasma-assisted combustion and plasma-chemical fuel reforming [5].

Comprehensive quantum chemical analysis with the usage of the second-order perturbation multireference XMCQDPT2 [6] approach was carried out to study the kinetic processes in the $N_2(A^3\Sigma_u^+)+H_2$ and $N_2(A^3\Sigma_u^+)+H_2O$ systems. The energetically favorable reaction pathways were revealed based on the exploration of potential energy surfaces. It was shown that the reactions $N_2(A^3\Sigma_u^+)+H_2$ and $N_2(A^3\Sigma_u^+)+H_2O$ occur with small activation barriers and, primarily, lead to the formation of N_2H + H and N_2H + OH products, respectively. Further, the interaction of these species could give rise the ground state $N_2(X\,^1\Sigma_g^+)$ and H_2 (or H_2O) products, however, the estimations, based on RRKM theory and dynamic reaction coordinate calculations, exhibited that the $N_2(A^3\Sigma_u^+)+H_2$ and $N_2(A^3\Sigma_u^+)+H_2O$ reactions lead to the $N_2(A^3\Sigma_u^+)$ dissociative quenching predominately. Appropriate rate constants for revealed reaction channels were estimated by using a canonical variational theory taking into account the tunneling and the effects of vibrational anharmonicity of transitions states and reactants. It was demonstrated that these rate constants are in reasonable agreement with known experimental data (see [7]). Besides, the obtained thermally equilibrium rate constants were partitioned into the state-specific rate coefficients to compare with measurements available in the literature [7, 8].

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